

Interactive comment on “Cloud droplet activation: solubility revisited” by L. T. Padró and A. Nenes

Anonymous Referee #2

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General Comments: This paper discusses an important aspect of understanding CCN behavior and specifically of reconciling difference between theoretical and observed CCN activation. It investigates the apparent ‘enhanced solubility’ of aerosol particles as CCN which has been observed by many experimentalists. The authors discuss the solubility enhancement using the concept of “Curvature Enhanced Solubility” which occurs due to the Kelvin effect (curvature) of extremely small solid particles suspended in a liquid. The authors of also conducted some experiments to derive necessary parameters to support the theoretical concepts. Overall, this is an important and useful addition to the discussion of CCN behavior of organic aerosols. For the first time, the hypothesis of increased organic solubility (compared to traditional bulk solubility) is investigated quantitatively. The ideas are novel and the paper is relevant to many readers of ACP. However, there are a few important details (described below) which should be addressed.

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Specific Comments: In the last sentence of the abstract, the authors list the third ‘important finding’ of the research to include the impacts of trace impurities on magnifying CES but this is only touched on briefly in the paper. This ‘finding’ should either be removed from the abstract or expanded upon in the paper itself (providing there is more experimental detail to properly evaluate it). The paper is sufficiently strong without inclusion of this finding and the reviewer suggests it be removed.

An important part of the paper is using the Kelvin equation (4) relating enhanced solubility to the size of the solid core. It should be clearly explained that this equation is not valid down to zero particle size (which would imply that nothing could ever crystallize out of solution). There is no defined ‘lower limit’ for the applicability of the Kelvin equation (that the reviewer is aware of) but definitely is not zero and therefore the equation should be used with caution.

On page 2335, line 1, the conclusion that “aerosol that is initially wet can retain its water at very low relative humidity”, while likely a true statement based on other work, does not follow or appear relevant to the current work. The current work is focusing on enhanced solubility inside a droplet and not equilibrium relative humidity. If the authors wish to discuss this, explanations of the solute effect on decreasing equilibrium water vapor pressure must be discussed in detail. This appears beyond the scope of the current paper. If the authors do include some commentary regarding ‘very low RH’ they should specify what that means: < 10%? <1%? Or even lower?

Equation (8) defines $\phi = n_s/n_{\text{bulk}}$. Assuming for a single-component species such as those studied here, $n_s/n_{\text{bulk}} = C_{\text{eq}}/C_{\text{bulk}}$ from Equation (4), then the critical nucleation size can be back-calculated from the values in Table 2. This leads to results for critical nucleus sizes between 0.004 nanometers and 0.05 nanometers to obtain the required solubility enhancement of Phthalic acid (using the authors data and ranging γ between 0.1 and 1.2 mN/n). This is beyond the reasonable applicable limits of the Kelvin equation for solubility enhancement and needs to be seriously addressed by the authors.

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Surface tensions were measured for bulk solutions but the point of the paper is that the solutions at activation may be many times supersaturated. What effect to the others believe this dramatic supersaturation will have on the true surface tension of a solution at activation?

Figure 5 and page 2338 compare the authors' measurements to a correlation by Söhnel (1982). It is the reviewers understanding that the this correlation was performed only for inorganics. If this is correct, the authors need to justify the use of this correlation to organic compounds. Regarding this same Figure 5, there are 4 data points from the current work which are not labeled. The authors only refer to leucine, azelaic, and phthalic acids so what is the forth point and which is which?

Page 2338, line 20 indicates the critical diameter was taken to be 5 nm - why was this value chosen? Since this is truly an unknown, it would be more thorough for the authors to vary this parameter.

Page 2338, lines 21-23 state that leucine was always dissolved and consistent with complete solubility seen previously by Raymond and Pandis (2002). Looking back at this paper, this is not what was concluded. In fact, R&P and later Huff-Hartz et al. (2006) determined leucine to behave as expected with very limited solubility and no CCN activity below 200-250 nm. This is a very important error in the paper that much be corrected and explained. From the data in Figure 6, it appear the authors believe that leucine activates at 84 nm diameter under 0.3% supersaturation. This is definitely not in agreement with R&P or HH or any other published data the reviewer is aware of. The data by R&P for leucine also appears to have been excluded from Figure 8.

Table 2 indicates all species show an increase in the ratio of required moles for activation at higher supersaturations but it is not clear to the reviewer why this would occur from a physical basis. Some discussion of this phenomenon is warranted. Also, the one exception to this pattern is leucine - why is the value at 1% SS significantly larger than that at 1.2% SS?

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Technical Corrections: Equation (1) is missing the density term in the first part of the exponential and also includes the osmotic coefficient in the second part which is removed from all remaining equations without any discussion.

In Figure 4, d_{core} is listed only as d_{c1} and d_{c2} while the text referring to this figure refers to $d_{\text{core,min}}$ and $d_{\text{core,max}}$. These should be brought into agreement.

Page 2333, line 17: adding the word 'initially' before 'unsaturated aqueous phase' would be more accurate and clear.

Text and figures use a combination of "undersaturated" as in line 5, page 2334 and "subsaturated" as in Figures 3 & 4. These should be consistent.

The values used for the calculations in Figure 3 and used in the text are (presumably) for Ammonium Sulfate and this should be mentioned for completeness.

Page 2337, line 8 states 'a flat substrate of compound'. What defines 'flat'. Because contact angle can vary based on surface topography, it would be useful to know (microscopic image, SEM image, AFM image, etc) what the surface looks like of different scales. Being organic crystals, the crystallization may produce many interesting and unforeseen topographies. Also, it should be noted that the 'flat' surface generated on the macro scale for these measurement may be very different from the 'true' surface on the nanoscale.

Page 2337, line 11 states that the smoothest surface was obtained starting with i_j saturation solutions. This does not make sense to the reviewer because, in order to crystallize out of solution, all solutions must transition thru saturation first. It should therefore not matter what the initial concentration was.

Page 2337, lines 25-27 imply that lack of variability between measurements and across a surface means that surface heterogeneities will not affect contact angle and thus may be extrapolated to the nanoscale. Again, this would not be true if macroscale was different than nanoscale.

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Page 2338, line 19 mentions sizes ranging from 10-500 nm but the only ones in Figure 6 are for 84, 92, and 114 nm.

Page 2339, line 13 says 'pinonic' while Figure 7a says 'pinic'. The authors should carefully check the use of these compounds since they are so similar and the reviewer may have missed other locations where the same error occurred.

Page 2339, lines 14-16 indicate a 'jump' in the critical saturation between 5 and 15 mN/m - this strikes the reviewer as odd and it might be useful to explain briefly why this jump occurs based on the equations used. This is somewhat confusing to the reviewer and an important point in the paper that deserves clarification.

Page 2341, lines 20-23 indicates that aggressive drying (heating) was used by Broekhuizen et al. (2004). The reviewer could find no mention of heating an aerosol stream for the purposes of drying in this paper.

Page 2342, lines 2-3 are confusing in their wording and reference a paper (Padro et al. 2007) which does not appear in the list of references.

Table 1 appears to be in no particular order and should be reordered in a logical fashion (alphabetical, by increasing solubility, etc.) and match the order of compounds in Table 2.

Table 2 uses more significant figures than are justified based on the uncertainties that exist. Two significant figures are likely all that is justified.

Table 3 mentions 'organic/organic solid-liquid' which does not make sense. It should also read 'interface' not 'interphase'.

The data for surface tension of solutions is significantly different from those published by Huff-Hartz (2006): Az = 59, Ph = 64, Leu = 70. The current paper lists almost all at 71.xx which strikes the reviewer as strangely consistent (all like pure water) and too precise.

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Figure 5 should label the compounds which are given for pink squares. How applicable is Söhnel to organics and surfactants?

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